## Title: <u>THERMODYNAMICS OF ELECTROLYTE SOLUTIONS FOR USE IN HIGH ENERGY LITHIUM BATTERIES</u>

**Principal investigator:** Dr. Angela F. Danil de Namor,
Laboratory of Thermochemistry,
Department of Chemistry,
University of Surrey,
Guildford, Surrey. GU2 5XH

**Postgraduate Students:** M.A. Llosa Tanco and Cho. Ng

A copy of the paper published recently in the Journal of Physical Chemistry is enclosed.

This report contains information regarding

a) Thermodynamic parameters for the complexation of 15-crown-5 and lithium salts at 288.15 K in order to assess the temperature effect on these processes.

b) Gibbs energies, enthalpies and entropies for the binding of lithium with 4'-nitrobenzo-15-crown-5 (Fig. 1) in acetonitrile at the standard temperature. This part of research aims to investigate the effect of substituents on the complexing abilities of 15-crown-5 and lithium cations.
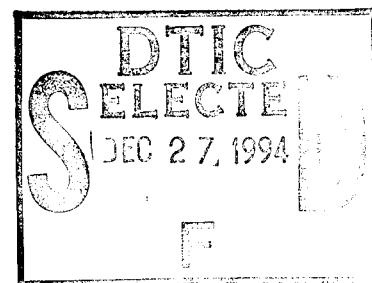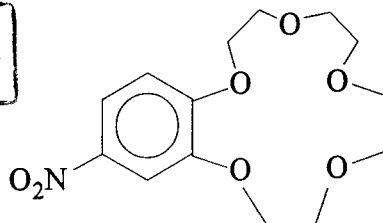
**Fig. 1.** 4'-nitrobenzo-15 crown 5

## a) <u>Thermodynamics of 15-crown-5 and lithium salts at 288.15 K</u>

### i) <u>Standard enthalpies of solution</u>.

Table 1 lists the standard enthalpies of solution, $\Delta_s H^\circ$ of 15 crown 5 in acetonitrile at 288.15 K and corresponding data for two lithium salts, namely, lithium tetrafluoroborate ($LiBF_4$) and lithium triflate ($LiCF_3SO_3$) in the same solvent.

**Table 1.** Standard enthalpies of solution of 15 crown 5, lithium tetrafluoroborate and lithium triflate in acetonitrile at 288.15 K

| Compound | Concentration range (mol.dm$^{-3}$) | $\Delta_s H^\circ$/ kJ.mol$^{-1}$ |
|---|---|---|
| 15 crown 5 | $2.24 \times 10^{-3}$ - $9.51 \times 10^{-3}$ | $-5.03 \pm 0.06$ |
| $LiBF_4$ | $2.53 \times 10^{-3}$ - $2.11 \times 10^{-2}$ | $-6.78 \pm 0.49$ |
| $LiCF_3SO_3$ | $7.09 \times 10^{-4}$ - $1.46 \times 10^{-2}$ | $-16.10 \pm 0.70$ |

Comparison of these data with values obtained for the $\Delta_s H^\circ$ of the same crown and the same electrolytes in acetonitrile at 298.15 K ( 15 crown 5, $\Delta_s H^\circ$ = -4.48 $\pm$ 0.16 kJ.mol$^{-1}$; $LiBF_4$, $\Delta_s H^\circ$ = -12.93 $\pm$ 0.89 kJ.mol$^{-1}$; $LiCF_3SO_3$, $\Delta_s H^\circ$ = -15.59 $\pm$ 0.82 kJ.mol$^{-1}$), shows that the enthalpy of solution is not affected by a change of temperature for 15 crown 5 and $LiCF_3SO_3$. However differences are found in the enthalpy of solution for $LiBF_4$.
In order to calculate the enthalpy of coordination of lithium and 15 crown 5 at 288.15 K in the solid state the determination of the enthalpy of solution of the lithium coronand electrolytes is in progress.

### ii) <u>Thermodynamic parameters of complexation of lithium salts and 15 crown 5 at 288.15 K in acetonitrile.</u>

Table 2 lists stability constants (log $K_s$) and derived Gibbs energies ($\Delta_c G^\circ$), enthalpies ($\Delta_c H^\circ$) and entropies ($\Delta_c S^\circ$) of lithium salts and 15 crown 5 in acetonitrile at 288.15 K

**Table 2.** Stability constants and derived Gibbs energies, enthalpies and entropies for the complexation of various lithium salts and 15 crown 5 in acetonitrile at 288.15 K

| Electrolyte | log $K_s$ | $\Delta_c G^\circ$ kJ·mol$^{-1}$ | $\Delta_c H^\circ$ kJ·mol$^{-1}$ | $\Delta_c S^\circ$ JK$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $LiAsF_6$ | 4.41 $\pm$0.04 | -25.15 $\pm$0.23 | -21.26 $\pm$0.70 | 13.1 |
| $LiBF_4$ | 4.40 $\pm$0.04 | -25.12 $\pm$0.22 | -22.82 $\pm$0.84 | 7.7 |
| $LiCF_3SO_3$ | 4.40 $\pm$0.03 | -25.10 $\pm$0.17 | -22.15 $\pm$0.65 | 9.9 |

The process of complexation is made by favourable enthalpy and entropy contributions as reflected in Table 2 and the data reported are quite independent of the anion which provide considerable evidence that both, the uncomplexed and complexed lithium salts are fully dissociated in this solvent.

Comparison of these data with values obtained at the standard temperature (298.15 K) (see Table 3) shows that the equilibrium data are not affected by a change of temperature. However differences are observed in the enthalpy and entropy contributions which needs to be carefully analysed by having data over a wide range of temperatures in order to gain full information and to determine variations in the heat capacity of these systems.

**Table 3.** Stability constants and derived Gibbs energies, enthalpies and entropies for the complexation of various lithium salts and 15 crown 5 in acetonitrile at 298.15 K

| Electrolyte | $\log K_S$ | $\Delta_c G^\circ$ kJ·mol$^{-1}$ | $\Delta_c H^\circ$ kJ·mol$^{-1}$ | $\Delta_c S^\circ$ JK$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| LiAsF$_6$ | 4.22 ±0.05 | -24.09 ±0.28 | -24.30 ±0.16 | -0.7 |
| LiBF$_4$ | 4.44 ±0.12 | -25.34 ±0.68 | -25.34 ±0.33 | 0.0 |
| LiCF$_3$SO$_3$ | 4.40 ±0.07 | -25.12 ±0.40 | -24.15 ±0.87 | 3.0 |

**b) Gibbs energies, enthalpies and entropies for the binding of lithium with 4'-nitrobenzo-15-crown-5 in acetonitrile at the standard temperature.**

Table 4 shows the data obtained for the different electrolytes and 4'-nitrobenzo-15 crown 5 in acetonitrile at 298.15 K

**Table 4.** Stability constants and derived Gibbs energies, enthalpies and entropies for the complexation of different lithium salts and 4'-nitrobenzo-15 crown 5 in acetonitrile at 298.15 K

| Electrolyte | $\log K_S$ | $\Delta_c G^\circ$ kJ·mol$^{-1}$ | $\Delta_c H^\circ$ kJ·mol$^{-1}$ | $\Delta_c S^\circ$ JK$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| LiAsF$_6$ | 3.91 ±0.06 | -22.32 ±0.34 | -20.52 ±0.74 | 6.1 |
| LiBF$_4$ | 3.81 ±0.06 | -21.77 ±0.36 | -20.26 ±0.72 | 5.0 |
| LiCF$_3$SO$_3$ | 3.66 ±0.13 | -20.89 ±0.72 | -20.82 ±1.07 | 0.2 |

Comparison of these data with values obtained for the complexation of the same electrolytes with 15 crown 5 in acetonitrile at 298.15 K (see Table 3), shows that there is a reduction in the enthalpy observed for 4'-nitrobenzo-15 crown 5 with respect to 15 crown 5, which can be attributed to the presence of the $NO_2$ group, which being a deactivating group in the aromatic ring, produce a decrease in the coordinating properties of the oxygen attached to the benzene ring. In terms of entropies there are not marked differences in the substituted crown relative to 15 crown 5. Therefore, the weaker stability of the complex reflected in the $\Delta_c G°$ values is due to a decrease in enthalpy.